PB81-226268

VOC Emission Control Technologies for Ship Painting Facilities: Industry Characterization

CENTEC Corp.
Reston, VA

Prepared for

Environmental Protection Agency
Cincinnati, OH

Jul 81

U.S. Department of Commerce
National Technical Information Service
NTIS

PB81-226268

EPA-600/2-81-131
July 1981

VOC EMISSION CONTROL TECHNOLOGIES FOR SHIP PAINTING FACILITIES

- Industry Characterization -

Prepared by

CENTEC Corporation
11260 Roger Bacon Drive
Reston, VA 22090

Project Officer
Charles H. Darvin
Nonferrous Metals and Minerals Branch
Industrial Environmental Research Laboratory
Cincinnati, OH 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-81-131	2. ORD Report	3. RECIPIENT'S ACCESSION NO. PB81 226268
4. TITLE AND SUBTITLE VOC Emission Control Technologies for Ship Painting Facilities		5. REPORT DATE July 1981 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. W. Meredith, M. Moskowitz, J. G. Kresky D. Harrison		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS CENTEC Corporation 11260 Roger Bacon Dr. Reston, VA 22090		10. PROGRAM ELEMENT NO. 1AB604 11. CONTRACT/GRANT NO. WE-2907-10
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Cincinnati, OH Office of Research & Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Mar. 1980 - Feb. 1981 Final 14. SPONSORING AGENCY CODE EPA600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The U. S. Environmental Protection has the responsibility of reducing the levels of VOC emissions from the nation's stationary and mobile sources. The project was directed at assessing the levels of VOC emissions from ship painting operations with the intent of determining the need for research activity in this industry. A secondary objective was to identify control technologies or new technology concepts which may be used or developed and demonstrated that lowers the levels of VOC emissions during ship painting. The investigators reviewed the literature and made direct contact with the ship building and repairing industry to develop their conclusions and recommendations on technology concepts.

On a combined basis the 76 largest shipyards in the U.S. were found to currently emit 41 to 95 metric Tons (45 to 105 short tons) of VOC into the atmosphere each operating day. Military painting account for approximately 50 percent of that volume. The technology approach for potentially reducing the VOC emissions levels are paint reformulation and increase transfer efficiency of the painting equipment.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Control Metal Finishing Volatile Organic Compounds	Metal Coating Painting VOC Emissions	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)*	21. NO. OF PAGES 22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the pollution related impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the results of an investigation into the control of solvent (VOC) air pollutant emissions from ship painting operations. The study was performed to quantify the volume of VOC released to the atmosphere from ship painting processes and to identify potential control concepts or allow more effective control of the VOC emissions. The results are being used within the Agency's Office of Research and Development as part of a larger effort to develop improved technologies for reducing pollutant discharges in the metal finishing and fabrication industries. The findings will also be useful to other Agency components and industry in dealing with environmental control problems. The Nonferrous Metals and Minerals Branch of the Energy Pollution Control Division should be contacted for any additional information concerning this program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This project was initiated to identify control technologies available or having potential for reducing the quantities of volatile organic compounds (VOC) emitted from ship painting operations. A second goal was to estimate the amount of VOC being emitted on a daily basis for the entire industry.

VOC emission control can be attained by any of three approaches:

1) Change paint formulations by either reducing or eliminating solvents, or create paints that last longer and therefore reduce the number of times a ship is painted with attendant VOC releases.

2) Improve the transfer efficiency by modifying paint application technologies.

3) Install add-on equipment that captures and destroys or reclaims the VOC.

The first two approaches are being actively pursued by the ship painting industry, primarily because of the economic benefits associated with them and not as part of a VOC reduction goal. The third approach (add-on equipment) has two major problems: the first is the nature of the operation which makes capture systems impractical and the second is the high cost.

There is no known use or consideration for use of add-on control equipment in this industry. Therefore further reductions in VOC emissions from ship painting will come from increased use of low solvent and/or high performance paints and/or increased transfer efficiencies. It appears that the development of higher performance paints will continue.

On a combined basis the 76 largest shipyards in the U.S. are currently emitting 27.9 to 65.3 metric tons (31 to 72 short tons) of VOC into the atmosphere on a daily basis (365 days/yr). Military ship painting accounts for about 50 percent of this amount.

This report was submitted in fulfillment of Contract No. WE-2907-10 between the U.S. Environmental Protection Agency and CENTEC Corporation, Reston, Virginia. This report covers the

period July 14, 1980 to April 14, 1981 and work was completed as of April 14, 1981.

CONTENTS

Section	Title	Page
	ABSTRACT	iii
	FIGURES	viii
	TABLES	ix
	ACKNOWLEDGEMENTS	x
	SECTION 1 INTRODUCTION	1
	SECTION 2 CONCLUSIONS	2
	SECTION 3 RECOMMENDATIONS	5
	SECTION 4 SHIPYARD PRACTICES RELATED TO PAINTING	
4.1	INDUSTRY DESCRIPTION	6
4.2	GENERAL PAINTING PRACTICES	7
4.3	GEOGRAPHICAL DISTRIBUTION	8
4.4	FREQUENCY OF PAINTING	9
4.5	QUANTITIES OF PAINT USED	11
4.6	TURN-AROUND TIME	12

CONTENTS
(Continued)

Section	Title	Page
	SECTION 5 MARINE PAINTS	
5.1	MAJOR PAINTS FOR MARINE APPLICATIONS . . .	13
5.1.1	GENERAL	13
5.1.2	ACRYLIC RESINS	14
5.1.3	ALKYD RESINS	17
5.1.4	EPOXY RESINS	18
5.1.5	POLYURETHANES	20
5.1.6	VINYL RESINS	22
5.1.7	CHLORINATED RUBBER	26
5.1.8	INORGANIC ZINC COATINGS	26
5.1.9	ANTIFOULING COATINGS	27
5.2	THE ROLE OF VOC IN PAINT	28
5.3	WATERBORNE PAINTS	33
5.4	TRENDS IN INDUSTRY	35
5.4.1	THE USE OF TWO-PART REACTIVE PAINTS	35
5.4.2	THE USE OF WATERBORNES	36
5.4.3	MARINE PAINTING RESEARCH	37
	SECTION 6 VOC EMISSION CONTROL TECHNOLOGIES	
6.1	INTRODUCTION	39
6.2	MODIFICATION OF PAINT FORMULATIONS	39
6.3	CAPTURE TECHNOLOGIES	41

TABLE OF CONTENTS
(Continued)

Section	Title	Page
6.4	EMISSION REDUCTIONS BY IMPROVING APPLICATION TECHNOLOGIES	42
6.4.1	OPTIONS FOR APPLYING PAINTS	42
6.4.2	SPRAY PAINTING TECHNOLOGIES	43
6.4.3	NEW TECHNOLOGY	47
	SECTION 7 ESTIMATION OF NATIONAL VOC EMISSIONS FROM MAJOR SHIPYARD PAINTING	50
	BIBLIOGRAPHY	56
	GLOSSARY	58

LIST OF FIGURES

Figure	Title	Page
6-1	Paint Spraying Systems	44

LIST OF TABLES

Number	Title	Page
4-1	Inventory of Major U.S. Shipyards	6
4-2	Inventory of Facilities at Major U.S. Shipyards	7
4-3	Concentrations of U.S. Shipyards	8
5-1	Comparison of Resin Systems	15
5-2	Areas of Application for Ship Paints . . .	16
5-3	Description of Organic Solvents Used in Marine Paints	29
5-4	Common Paint-Solvent Systems for Marine Applications	32
5-5	Percent Solids by Type of Paint	33
5-6	Two-Part Reactive Paint as Percent of Total Paint Use	36
5-7	Waterborne Paint as Percent of Total Paint Use	37
6-1	Solvent Proportions by Type of Paint . . .	40
7-1	Paint Use and Employment at Shipyards Visited	51
7-2	Estimated VOC Emissions from Painting at Major Shipyards	53
7-3	Summary of VOC Emission Estimates	55

ACKNOWLEDGMENTS

The authors would like to thank George S. Thompson, Jr., Branch Chief, and Charles H. Darvin, Project Officer, Nonferrous Metals and Minerals Branch, Industrial Environmental Research Laboratory, Cincinnati, Ohio for their direction and assistance during this project. Acknowledgment is also due Edward Vincent of EPA's Office of Air Quality Planning and Standards for his direction and review of the project. A special thank you goes to the Environmental Committee of the Shipbuilders Council of America chaired by George Curtis III for invaluable assistance in providing data, arranging for site visits, and reviewing the draft report.

SECTION 1

INTRODUCTION

The primary objective of this study was to identify technologies that serve to reduce volatile organic compound (VOC) emissions from ship painting operations and to perform a preliminary evaluation of these technologies. Another objective was to define the sources and characteristics of the VOC emissions. As this investigation was primarily interested in the painting of very large structures, only shipyards with facilities for vessels 91.4 meters long (300 feet) and 1814 metric tons (2000 short tons) or over were considered.

Conversations with relevant trade associations led to contacts with individual paint formulators, painting equipment manufacturers, and shipyards. Based on these contacts, site visits, and the literature, an understanding of the industry and its flexibility and constraints with regard to VOC emission control was developed. The site visits accomplished constitute a national sample of shipyards from the defined population. Information obtained during these visits has allowed a statistical determination of total nationwide VOC emissions from major shipyards.

To aid the reader in understanding the industry, this report includes a section on general shipyard operating procedures with regard to ship painting. As the source of the VOC emissions is the paint, a detailed section on marine paints is included. Common control technologies are evaluated as to their relevancy to ship painting and some innovative technologies are described in detail. In all sections, industry trends observed are noted. The report concludes with a section in which VOC emissions from ship paint operations nationwide are estimated.

SECTION 2

CONCLUSIONS

Approximately 63.5 metric tons (70 short tons) of volatile organic compounds (VOC) are being emitted daily from the 76 largest shipyards in this country. The source of the VOC is the organic solvents present in the paint formulations and also solvents used for thinning paint and cleaning painting equipment.

Marine coatings are absolutely vital for protecting the ships from corrosive and biotic attacks from the ship's environment. There are many marine paints serving specific functions such as corrosion protection, abrasive protection, and antifouling. Numerous types of paints can serve the same functions and each may use different solvents at various volume percents. Ship owners and paint formulators specify the paints and coating thicknesses to be used at shipyards.

The major U.S. shipyards are scatterd along the east, west, and Gulf coasts with a few inland waterway sites and island locations. Yards designed primarily for repair consume considerably more paint and therefore generate more VOC emissions than yards that do primarily construction of new ships. Specific paint selections are based on the intended use of the ship, ship activity, travel routes, desired time between paintings, the aesthetic desires of the ship owners, and fuel costs.

VOC emission control can be attained by any of three approaches:

1) Change paint formulations by either reducing or eliminating solvents or create paints that last longer and therefore reduce the number of times a ship is painted with attendant VOC releases.

2) Improve the transfer efficiency by modifying paint application technologies.

3) Install add-on equipment that captures and destroys or reclaims the VOC.

The first two approaches are being actively pursued by the ship painting industry, primarily because of the economic benefits associated with them and not as part of a VOC reduction goal. The third approach (add-on equipment) has two major problems: the first is the nature of the operation which makes capture systems impractical and the second is the high cost.

Although high performance coatings will always cost more initially, their life-cycle costs may be significantly better than that of conventional coatings. As a visit to a drydock can cost more than $100,000 per day, ship owners want to minimize the frequency of these visits, and continuous development of technologies that can help achieve this desire is likely.

The consensus of the environmental committee of the Shipbuilders Council of America is that while the painting of U.S. Navy ships accounts for approximately 30 percent of marine paint consumption it is likely to be responsible for 50 percent of the VOC being emitted. The reason for this is that the military specifications for paints have not kept up with the state-of-the-art and require extensive use of high solvent paints.

An analysis of the data collected during this study allows the following specific conclusions to be made:

1) The nature of ship painting necessitates extensive use of the most inefficient paint application technique--spray painting.

2) There is a definite trend toward higher utilization of airless paint spraying as opposed to air spraying. This is due to airless spraying's higher transfer efficiency, ability to spray higher solids paint, and ability to spray a thicker coat per pass.

3) Conventional control technologies, such as capture and destroy systems, are not applicable to shipyards for major technical and economic reasons.

4) U.S. shipyards painting large ships on a combined basis are currently emitting between 40.8 and 95.3 metric tons (45 and 105 short tons) of VOC per day (250 days per year). This is equivalent to a range of 27.9 to 65.3 metric tons (31 to 72 short tons) based on 365 days per year which is more realistic for many shipyards. Military ship painting accounts for about 50 percent of the VOC being emitted.

5) Costs are forcing the industry to reduce VOC emissions. This conclusion is illustrated by trends in industry toward the use of high solids and high performance paints, and paint application techniques with higher

transfer efficiencies. These trends reduce VOC emissions as a welcome but not intentional side benefit in most cases.

6) There is no known use or consideration for use of add-on control equipment in this industry. Therefore further reductions in VOC emissions from ship painting will come from increased use of low solvent and/or high performance paints and/or increased transfer efficiencies. It appears that the development of higher performance paints will continue.

EPA Form 2250-4 (4-90)
(PREVIOUSLY CIN: EPA FORM 2571)
TYPING GUIDE SHEET

SECTION 3

RECOMMENDATIONS

In order that shipyards may make decisions related to ship painting based on sound empirical data rather than estimates, it is recommended that the EPA conduct studies investigating the true transfer efficiencies of the various coating application technologies. It is anticipated that this type of data would allow quantification of paint losses and therefore provide an economic basis upon which shipyards can make decisions. This would accelerate the trend toward more efficient technologies with their attendant lower VOC emissions. The Docknight™ painting system described in this report is specifically recommended for a transfer efficiency type of evaluation as it has direct application to ship painting operations.

It is further recommended that EPA publish a report on both high solids and high performance coatings that are useable by the ship painting industry. The report should highlight benefits, dispel myths, and encourage the use of these coatings in lieu of coatings which either have higher VOC content or require more frequent paint applications.

The large relatively flat surfaces on a ship's hull would be likely candidates for roller coating if the proper technology could be developed. Roller coating has a nearly 100 percent transfer efficiency and would likely result in reduced VOC emissions. It is recommended that a research and development program investigate the design and feasibility of a mechanical roll coating system suitable for painting the hulls of ships.

SECTION 4

SHIPYARD PRACTICES RELATED TO PAINTING

4.1 INDUSTRY DESCRIPTION

The Maritime Administration[9] lists 76 U.S. shipyards that qualify as Code A shipyards, meaning that they have facilities capable of handling vessels 91.4 meters long (300 feet) or longer and weighing 1814 metric tons (2,000 short tons) or more. As the focus of this study is on the VOC emissions associated with the painting of large ships, it is these 76 yards and their painting practices that provided most of the data for this report. These shipyards can be divided into three categories based on their capabilities as follows:

1) Construction facilities only

2) Repair facilities with construction capabilities, or

3) Repair facilities only

The national inventory of these large shipyards (those having facilities to either build or drydock ships of over 91.4 meters (300 feet) in length or over 1814 metric tons (2,000 short tons) by category is shown in Table 4-1.

Table 4-1

Inventory of Major U.S. Shipyards

Shipyards without repair capabilities	3
Combination of construction and repair facilities	47
Repair facilities without construction capabilities	26

The actual type of facilities for doing the building or repair work at these yards is listed in Table 4-2.

Superscripts refer to items in the Bibliography, p. 56.

Table 4-2

Inventory of Facilities at Major U.S. Shipyards

Building positions on land	83
Graving docks	79
Floating drydocks	76
Marine railways	6
Buildings for shipbuilding	7
Mechanical lifts	1

It is difficult to classify many facilities into either a shipbuilder or ship repair category as many shipyards are engaged in both shipbuilding and repair/maintenance in various degrees. The percentage of work mix varies widely throughout the industry as well as from year to year at a single shipyard. The quantities and specific types of paint used in facilities primarily engaged in shipbuilding differ from those used at repair facilities and therefore the functions of the shipyards' facilities is important to this study.

4.2 GENERAL PAINTING PRACTICES

Shipbuilding includes painting the entire ship, both the interior and exterior. The inside areas include living spaces, machinery spaces, cargo spaces, tanks, and voids. After the ship is added to the owner's fleet, coatings on the decks, superstructure, and most interior spaces are maintained by the ship's crew while the ship is either in port or underway. The percentage of this type of painting depends on the vessel use (i.e., cargo or passenger), type of cargo and location of the ship's travel routes.

There are noticeable differences between painting a ship during construction and repainting as commonly done by repair facilities. Since it may take 1 to 3 years to construct a ship, painting is necessary to avoid corrosion during construction as well as being an obvious part of the finished product. Shipbuilders usually begin applying a paint system at the initial stages of construction. As steel plates are moved into the area where sections or modules are to be built, the plates are routinely cut to specifications, shot peened to remove mill scale, and primed as the module is being built. Sections are constantly being reblasted and repainted until they are fitted together and paint can be applied to the complete hull and other areas. The internal areas of the sections are coated quite often before the sections are joined. The total painting system of a new ship typically costs as much as 15 percent of the total purchase price.

Repair yards having drydock facilities are generally involved with repainting of hulls. This is a convenient time for repairs to be done simultaneously on propulsion systems, steering systems, or whatever else is necessary. The work usually consists of blasting the hull and applying paint. Surface preparation is done to various degrees, ranging from a light blasting through commercial blasting to white metal blasting depending on the ship owner's specifications. Military vessels commonly receive white metal blasting at drydock visits. The hull then typically receives three paint systems: a primer; a mid-coat; and a topcoat. The keel is coated with the highest amount of antifouling additives in its topcoat. The area between the waterline when empty and the waterline when carrying a full cargo load is painted with less antifoulant, and the free-board area is painted with the least amount of antifoulant. The reason behind the judicious use of antifoulant is cost. Keel paint containing the highest concentrations of antifoulant typically costs as much as $13.20 per liter ($50 per gallon).

4.3 GEOGRAPHICAL DISTRIBUTION

Although the majority of shipyards are located on the seacoast, there are a few yards located in the Great Lakes and on major navigable rivers such as the Mississippi.

Table 4-3 shows the 10 areas and their associated port groupings into which the United States is divided. Also shown is the number of Code A shipyards in each area. Shipyards with topside only facilities were not considered.

Table 4-3
Concentrations of U.S. Shipyards

Area	Port Groupings	Code A Shipyards
West Coast 1	Seattle-Tacoma, Portland, Alaska	8
West Coast 2	San Francisco Bay, Hawaii	7
West Coast 3	San Pedro-Los Angeles, San Diego	5
Inland Waterways		3
Great Lakes		6
East Coast 1	Portland-Bath, Portsmouth, Boston-Quincy-Newport, Groton, Conn.	7
East Coast 2	New York, Camden-Philadelphia-Wilmington, Baltimore, Norfolk-Newport News	18
East Coast 3	Wilmington, N.C., Charleston-Savannah, Jacksonville-Miami	6
San Juan, P.R.		2
Gulf Coast Area	Tampa-Panama City, Mobile-Pascagoula, New Orleans, Texas	14

Eight shipyards in Virginia, Louisiana, Texas, California, Florida and Washington were visited to gather data for this study.

Regional climatological differences are important factors in the use of paint during the colder months of the year. While shipyards in Southern California, for instance, are able to paint most of the year, shipyards in the northern New England states may experience substantial periods of unsuitable painting weather due to freezing conditions. Northern shipyards sometimes alleviate this situation by sending ships to southern ports during inclement weather conditions for painting. The impact of these actions is that during the winter months VOC emissions from ship painting will increase in the south and drop in the north.

The use of certain solvents due to weather is another geographical factor. An example is the occasional use of alcohol as a solvent additive to waterborne zinc primer in colder weather.

Great Lakes shipyards generally do not conduct short term repairs during certain winter months due to poor painting conditions and the inability to move ships because of ice. In recent years, Great Lakes shipping has been halted during winter months because Coast Guard icebreakers have reduced service to the Great Lakes.

As opposed to ships operating in and subject to saltwater attack, there are little or no antifoulants applied on ships operating in the Great Lakes. In addition, paints used in Great Lake shipyards and inland waterway shipyards are not required to contain the same anti-corrosive agents as paints used on ocean-going vessels.

4.4 FREQUENCY OF PAINTING

The amount of VOC emissions as a result of ship painting will vary directly with the number of times the ship is painted over its lifetime. It is therefore important to understand the considerations involved in determining the time between ship paintings. The predominant factors are:

1) Geographical operation of the ship

   a) Ocean versus fresh water

   Saltwater is more aggressive toward metals than is freshwater and, therefore, lessens the time between paintings. The constituents of the paint applied are also affected. Ships used exclusively in the Great Lakes, such as iron ore carriers, generally are not

coated with antifoulants because of the absence of barnacles in fresh waters. The major problem is corrosion of the hull, whereas with oceangoing vessels the major problem is biotic fouling below the water line.

b) Tropics versus colder climates

Temperature influences biotic fouling. Ships mainly operating in the upper latitudes encounter less fouling due to slow biotic attack and a slower rate of chemical attack than do ships operating in the tropical regions.

2) Type of paint used in previous painting

The type of paint previously used may determine whether a ship can be painted over with a light surface cleaning or must be blasted heavily prior to painting. The cost of blasting is an important economic factor in deciding which paints to use as it may account for as much as 70 percent of the total resurfacing cost.

3) Type of service (e.g., cargo or passengers)

The type of cargo hauled relates to the amount of painting that can be performed while the ship is underway. For example, passenger cruise ships will not be painted to the extent that an oil or a cargo ship will be while underway. This means that more painting must be done during drydock time for cruise ships, whereas cargo vessels may drydock only to get a hull painting while the remainder is done by ship's hands. Painting underway represents a very small portion of the maintenance painting done.

4) Owner's maintenance schedules

The owner's maintenance schedule influences time between paintings. A scheduled maintenance of ship's equipment may coincide with paintings. An owner may not be vitally interested in the aesthetic value of a new painting on an older ship and may lengthen time between paintings. Conversely, a large oil company may repaint its flagship often.

5) Military versus civilian painting requirements

Military versus civilian painting requirements differ. The military will use military standard hull coatings and frequently blast to white metal when drydocked. Ship's hands constantly repaint the remainder of the ship while in port. Also, fleetwide times between paintings for various classes of ships have been adopted whereas private

shipowners decide painting schedules on an individual basis. Military ships routinely use as much as 5 times the antifoulants in hull paint as do civilian ships.

6) Percentage of time a ship is underway

The amount of time a ship spends underway also influences the time between hull paintings. If a ship is actively transporting cargo from port to port and spends little time waiting to on-load or off-load cargo, it is less subject to fouling as compared with a ship that may be at anchor for considerable lengths of time. Prime examples of this are naval vessels which frequently spend large amounts of time in port.

7) Use of cathodic hull protection

Many ships have cathodic anticorrosion systems. If operating properly, they extend the time period between hull paintings. The cathodic system can, if operating improperly, destroy a paint system by operating on excessively high currents. Metal castings, such as zinc alloy, are electrically connected to the ship's hull and act as sacrificial anodes. The anodes corrode preferentially to the iron hull of the ship. Silty water will frequently abrade paint from the hulls of ships and without cathodic protection the ship would have to be drydocked immediately or suffer severe corrosion problems.

8) Cost of fuel

The cost of fuel indirectly affects the time between hull paintings. Since fouling creates a hydrodynamic drag on the hull, a barnacle-laden ship will use more fuel and travel slower than a recently painted ship making the same voyage. With the ever increasing cost of fuel and costs of operating a ship, many owners drydock their ships for barnacle removal and repainting more frequently. One other option is to use more expensive high performance antifouling paints to prolong periods between paintings. The net impact of higher fuel costs is to increase the frequency of drydock visits.

4.5 QUANTITIES OF PAINT USED

When a ship is to be drydocked for maintenance and/or a hull repaint, the ship's owner usually provides the hull paint. In the case of the military, the yard supplies paint formulated to military specifications which is generally a low solids type. The civilian ship owners are generally represented by paint manufacturers' representatives who oversee the cleaning,

surface preparation and painting of the ship. The paint representatives act as QA/QC personnel to assure the work is performed in an acceptable manner. Factors considered in determining the amount of paint on a ship include: the type of paint, paint manufacturers' requirements, and the size and design of the ship.

Type Of Paint

The type of paint influences the thickness of the application. For example, a two-component, zinc-rich, pure epoxy may require a wet film thickness of approximately 50 microns (2 mils) whereas a bituminous coating usually used in voids may require a wet film thickness of 500 microns (20 mils). This represents a volume difference of 1000 percent.

Size and Design of Ship

The design of a ship is a factor in the amount of paint required. Ships with a "V"-shaped hull may have less surface area than a ship with a bulbous-shaped hull. Design also affects the relative quantities of the different types of paints used. The amount of freeboard, for example, influences the amount of anti-fouling paint versus freeboard paint used.

4.6 TURN-AROUND TIME

A typical ship may enter a drydock and leave within 5 to 10 days if no major repair work is necessary. Ships typically receive both maintenance and a hull blasting and repainting, which is referred to as a "shave and a haircut", while in drydock. Since the ship is completely out of the water, repairs can be carried out on equipment otherwise not accessible. The overall cost to the ship's owner of drydock time is very high because costs include not only drydocking and shipyard labor fees, but also loss of income for the ship due to inactivity. With costs running between $5,000 and $100,000 per day, ships are moved through a drydocking period as quickly as possible. Many shipyards operate around the clock for efficient use of time and facilities. It is not unusual for a shipyard to service 70 or more ships in one year.

SECTION 5

MARINE PAINTS

5.1 MAJOR PAINTS FOR MARINE APPLICATIONS

5.1.1 GENERAL

The source of VOC emissions from ship painting facilities is, of course, the solvents in the paints utilized. All of the solvents present in paint evaporate during either the application of the paint to the surface being coated or the curing process, to become what are known as VOC emissions. Conventional, off-the-shelf paints vary in solvent content from 20 to 82 volume percent, while special paints may contain as little as 5 volume percent solvent. Using very low solvent paints to reduce VOC emissions is an attractive approach to solving the problem; however, it has limited application in ship painting. This section discusses the various paints used to paint ships, their specific uses and the organic solvents associated with them, to aid the reader in understanding some of the paint related constraints shipyards are under with regard to VOC emissions control.

Marine paints play a vital role in a ship's overall performance. The paints have two purposes, to beautify and to protect the ship from corrosion. Due to severe environments, marine paints have to be high performance coatings. These high performance coatings are formulated to meet specific factors such as, location of the shipyard, application techniques, time of year when painted, condition of the surface to be painted, interval between maintenance, and type of service of the vessel.

Originally, paints used drying oils and natural resins as the binders. Now, most coatings used in the painting of metal surfaces are based on synthetic resins. Generally, synthetic resins are binders that are complex, long-chain substances. The choice of resin usually determines the possible means of application and cure. Certain coatings require specific temperatures to cure properly while others must be heated prior to application. Some coatings require humidity to cure while others do not. Humidity is of great interest to the industry, since it influences the final decision as to which paint will or can be

used. The solids content of paints is also of great interest to ship painters as coatings with higher solids contents have numerous cost and environmental benefits over coatings with high solvent contents. Commonly used paints in the ship building and maintenance industries are acrylics, alkyds, epoxies, polyurethanes and vinyls. These and other paints are discussed in subsequent paragraphs. Tables 5-1 and 5-2 provide comparisons of different marine coatings.

5.1.2 ACRYLIC RESINS

Acrylic paints contain from 52 to 68 volume percent VOC. One liter (0.26 gallon) of this paint would contain 0.52-0.68 kg (1.1-1.5 pounds) of VOC.

Acrylic paints are mainly used inside of the ship. Areas of application include internal decks, internal bulkheads, voids, and painted surfaces inside the engine room.

In general, acrylics are pale in color, have a fairly high tolerance for heat and display good uniformity and retention of color and gloss, even upon exposure to heat, sunlight, and ultraviolet light. Acrylic coatings offer one of the best protections against chalking and discoloration. For this reason, acrylics are used primarily as a topcoat over other coatings. They are suitable when thin films are required without a primer. Acrylics can be used in combination with other resins such as epoxies, vinyls, and chlorinated rubbers. This results in good adhesion and resistance to chemicals, corrosion, and impact.[2,5]

Acrylics can be formulated to be either thermoplastic or thermosetting in either a waterborne or solvent-borne* system. They also can be used as high solids coatings.

The following list illustrates some of the properties of acrylic paints for coating metals.

- Waterborne - Thermoplastic
  - Long-term protection in mildly corrosive environment
  - Excellent appearance
  - Low odor, low toxicity

---

*Solvent-borne is used in this report to mean organic solvent borne.

Table 5-1

Comparison of Resin Systems

Physical State of Coatings	Anti-fouling	Acrylic	Inorganic Zinc	Alkyd	Epoxy	Urethane	Vinyl	Chlorinated Rubber
Water-borne								
- Thermoplastic		X					X	
- Thermosetting		X	X	X	X			
Solvent-borne								
- Thermoplastic	X	X			X	X	X	X
- Thermosetting		X	X	X	X	X		
High Solids		X		X	X	X	X	
2-Component System			X		X	X		
Possible Use of Coating								
Primer		X	X	X	X	X	X	X
Final Coat	X	X		X	X	X	X	X
Undercoat	X			X				X
Method of Application								
Roller	X		X	X		X		
Air Spray	X	X	X	X	X	X		
Airless Spray	XX	XX	XX	XX	XX	XX	XX	XX
Brush	X		X	X				
% of Total Use*	12.4	4.9	5.1	31.9	29.0	4.1	4.2	6.2

X = Observed or reference found

XX = Most common method

Blank = No reference found

* Figures represent data for the state of California in 1976. Solvent use is not included.

Table 5-2

Areas of Application for Ship Paints

Where Used	Acrylic	Alkyd	Epoxy	Polyurethane	Vinyl	Chlorinated Rubber
Superstructure		X	X	X	X	X
Topside Equipment		X	X	X	X	X
Decks		X	X	X	X	
Hull-above water line		X	X	X	X	X
-below water line			X	X	X	X
Internal Decks	X	X	X	X		
Internal Bulkheads	X	X	X	X		
Voids	X	X	X	X		
Engine Room-surfaces	X	X				
-machinery						
Tanks			X	X	X	
Cargo Holds-wet			X	X		
-dry			X	X	X	

- Cleanup accomplished with water
- Nonflammable

- Waterborne - Thermosetting
  - Useful as primer or topcoat
  - Excellent adhesion, flexibility and chemical resistance
  - Outdoor durability
  - May require infrared cure in some cases
- Solvent-borne - Thermoplastic (Lacquers)
  - Can be used as a clear solution
  - Can be used as the basis for pigmented coating
  - Excellent durability
- Solvent-borne - Thermosetting (Enamels)
  - Good gloss and color retention
  - Application of higher solids than thermoplastics
  - Greater chemical resistance than thermoplastics
  - Outdoor durability is variable
- High Solid - Excellent hardness and gloss make it suitable for use on metal.

5.1.3 ALKYD RESINS

VOC's associated with alkyd paints are mainly mineral spirits and range in composition from 40 to 65 volume percent of the paint. One liter (0.26 gallon) of this paint would contain 0.36-0.58 kg (0.8-1.3 pounds) of VOC.

Alkyd resins are one of the more popular resins for ship painting and are used in a wide array of painting products. Alkyd coatings can be applied to large portions of a ship--inside and out. Areas of application include the superstructure, topside equipment, weather decks, hull, internal decks, bulkheads, voids, and painted surfaces inside the engine room. They are moderate in cost and fairly durable. Many are thermosetting, since they usually dry by reacting with air. Their versatility and high degree of compatibility with many

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 1371)
TYPING GUIDE SHEET

drying oils (limited primarily to short oil types for painting metal surfaces) and other synthetic resins, increases their usefulness. Alkyds, in combination with other resins, produce good adhesion, good heat resistance, and color retention. They are often used as primers, undercoats, and topcoats for metals. Alkyds may be formulated as water- or solvent-borne paints making them amenable to application by brush, roller, air spray, and airless spray.[2,5]

Entirely waterborne alkyd resins are bound by ester linkages that are relatively weak. This makes them susceptible to breakdown by weather, water, and chemicals. Also, the average molecular weights of alkyd compounds are low compared to other polymers, resulting in lower performance properties.

Solvent-borne alkyds, which are used most frequently in painting metal surfaces, use mineral spirits in a range of 40 to 65 volume percent as solvent. Alkyds are cured by an oxidizing reaction (thermosetting) and are useful as primers and undercoats.

Alkyds may be modified with phenolic resins, styrene, vinyl, toluene, acrylic esters, silicone intermediates, and other resins, to enhance certain qualities. For example, silicone intermediates will contribute added heat resistance and durability and as little as 5 percent melamine-formaldehyde resin will lessen curing time and increase hardness.

The versatility of alkyd resins also allows alkyds to modify other resin systems. Non-oxidizing alkyds are used as plasticizers in nitrocellulose lacquers, while thermoset acrylic resins are used in highly color retentive baking enamels. Occasionally, a small amount of an oxidizing alkyd will be used to supplement these systems.

In summary, alkyds find many uses in ship painting because of their cost, versatility, and compatibility with other resins. See Table 5-1 for a comparison of resin systems.

5.1.4 EPOXY RESINS

VOC's used with epoxy paints are xylol, n-butyl alcohol, naphtha, butyl alcohol, and aromatic hydrocarbons. These compounds range in composition from 20 to 79 percent (vol.). One liter (0.26 gallon) of this paint would contain 0.18-0.71 kg (0.4 to 1.6 pounds) of VOC.

The many types of epoxy resins possible increase their versatility. They are a preferred coating because of their superior solvent, detergent, corrosion, and chemical resistance, and high mechanical strength. These properties make epoxies extremely

well suited to application on the superstructure, topside equipment, decks, hull, voids, internal decks and bulkheads, tanks, and cargo holds. On their own, however, their resistance to heat and ultraviolet light is limited and epoxies must therefore be used in conjunction with another coating.[2,5]

Epoxies cure by chemical means. This allows for polymerization of the epoxies to proceed from the relatively low molecular weights of the coating "as applied" to the high molecular weight polymers in the "final film," which characterize their superior film properties. They can be formulated as water- or solvent-borne systems, or as high solids coats. They may be applied using most methods. The compatibility of epoxies with other resins further enhances their utility and popularity. As a group, epoxies are compatible, in varying degrees, with amino resins (melamine and urea formaldehyde resin); phenolic, vinyl, and certain acrylic resins; and short-oil, non-drying alkyds. They can be enriched with zinc to give galvanic protection or modified with silicone intermediates for added heat resistance.

Epoxy systems useful for painting metal surfaces are primarily amine-cured and polyamide cured. These are discussed below:

- Amine Cured Systems

  As a two-component system with the curing agent added just before use, they are specifically useful as heavy duty coatings. Sometimes they can be used with little or no cure.

  The properties include good chemical resistance, toughness and durability. This makes amine-cured epoxies excellent for lining tanks. Amine-cured epoxies can be formulated to very high solids levels thus reducing the number of coats required.

- Polyamide Cured Systems

  These resins are unique among epoxies in that they are thermoplastic, yet they produce topcoat films that are tough and flexible, chemical and abrasion resistant, and have good adhesion. They also are useful as primers because they give a high degree of adhesion. Because they have the ability to cure at room temperatures and dry rapidly, separate curing of this primer sometimes can be eliminated with both primer and topcoat curing together. In addition, because this primer has high molecular weight and inherent superior corrosion resistance, further savings can be realized by reducing the required film thickness. Common solvents for these thermoplastic systems are xylol, butyl alcohols, aromatic hydrocarbons (e.g., xylene and toluene), and naphtha.

In ship painting, these coatings are generally used on the exterior hull as an anti-corrosive coating from the light load line to the rail and also as a tank coating. With its superior resistance to chemical and mechanical wear, this system is commonly used on decks of ships carrying solvents.

5.1.5 POLYURETHANES

VOC's associated with polyurethanes are Cellosolve™ acetate, ethyl amyl ketone, and methyl n-butyl ketone. These compounds comprise from 45 to 56 volume percent of the paint. One liter (0.26 gallon) of this paint would contain 0.44-0.54 kg (0.98 to 1.2 pounds) of VOC.

Urethanes as a group are used in ship painting and noted for their toughness, flexibility, high abrasion and solvent resistance, weatherability, good adhesion, hiding power, gloss, and color retention qualities. These properties make urethanes extremely well suited to application on the superstructure, topside equipment, decks, hulls, voids, internal decks and bulkheads, tanks, and cargo holds. Urethanes can be applied at high solids content and can be cured at low temperature, 7°C (45°F). Polyurethanes are in use as primers and intermediate coats.

Urethane resins are the foremost film-forming type of polyurethane. They can be formulated as either enamels or lacquers, i.e., thermosetting or thermoplastic. Another polyurethane resin is based on the reaction with water or moisture in the air. This class of polyurethane is known as "moisture cure" and, to varying degrees, is the basis for two-component (or package) systems that result in linear polyurethanes. The previously mentioned polyurethanes produce linear polyurethanes with varying cross-linkages. Higher functional polyols in the urethane paints can be used to achieve a specific degree of cross-linking resulting in harder, and less flexible coatings.[2]

Three basic types of polyurethane systems will be discussed. They can be categorized as being oil modified, moisture cured (one package), or two-component system.

- Oil modified urethanes are most similar to conventional finishes. They are analogous to alkyd manufacture, where a drying oil is reacted with a polyhydric alcohol. Cure is achieved by oxidation. Metallic catalysts (typically cobalt, manganese, and lead) can aid drying while maintaining a resistant film.

- Moisture cure polyurethanes are typically one-package systems and are useful for coating metal. The urethane

as applied reacts with moisture to cure. This process may be enhanced by added heat cure. Solvents for these urethanes, which consist of 40 to 60 volume percent solids, are ketones, esters, aromatic hydrocarbons: specifically methyl n-butyl ketone, butyl acetate, ethyl amyl ketone, monoethyl ether acetate (Cellosolve™ acetate), xylene, toluene, and some methyl ethyl ketone and ethyl acetate. Although cure is possible under ambient conditions as well as at elevated temperatures, time limitations in application usually requires the addition of catalysts, typically organometals (such as cobalt, lead or tin), or amines. The catalysts effect rapid cure and protect the outstanding film properties of urethanes, making them useful as a single, final coat. High performance polyether based urethane coatings are most useful for metal surfaces. These coatings may be applied by roller and air or airless spray. Their rate of cure is dependent on the amount of moisture in the air.

- Two-component (package) systems are gaining in popularity for coating metal because of increasing energy costs and the possibility of eliminating or decreasing cure time and/or temperature. These urethanes on their own are not particularly good film formers so a second component is added as a coreactant. Any coreactant of suitable molecular weight can be used. Common coreactants are polyether, polyester, and castor oil.

  Typical solvents for two-component systems are cresylic acid, Cellosolve™ acetate, and diacetone alcohol with toluol and xylol employed as diluents. These urethanes must be mixed just prior to application, since they have an average pot life of 6 to 8 hours. These coatings then may be applied with standard air or airless spray equipment. These coatings may contain toxic isocyanates; however, this problem is minimized by the use of nonvolatile polymers rather than free isocyanate and has not detracted from the use of this paint system. Air supplied respirators should be on hand and overspray should be carefully controlled.

  Film thicknesses of 25.4 to 50.8 microns (1 to 2 mils) are common, with the coating applied at up to 80 percent solids content. Two-component urethane systems often are used as primers as well as final coats because of their high ultraviolet protection. Urethanes have excellent adhesion and will adhere to almost anything except oily surfaces.

Although their principal disadvantage is a 30 percent higher cost than some other coatings systems, two-component systems give improved coverage and offer solvent emission reduction. Most two-component urethane systems are suited for air curing if little or no drying heat is available, the major considerations being speed of any following operations. The rate of cure also can be affected by the addition of catalysts to the coating, such as amines for room temperature cure, or tin based organo-metallics for intermediate temperatures.

5.1.6 VINYL RESINS

Vinyl paint solvents range from 53 to 82 volume percent of the paint. One liter (0.26 gallon) of this paint would contain 0.48-0.73 kg (1.1 to 1.6 pounds) of VOC.

Vinyl coatings are used primarily by the Navy as anticorrosive and antifouling coatings. Vinyl coatings can be applied to a ship's hull, cargo holds, tanks, weather decks, superstructure, and topside equipment.

Vinyl resins were among the first addition polymers to be synthetically made and used in industry. Chemically speaking, vinyls may include all polymers made from monomers containing the vinyl group ($H_2C = CH -$) and, therefore, could include not only the common vinyl chloride, vinyl acetate, vinyl fluoride, and vinylidene chloride polymers and copolymers (which will be discussed in detail) but also polyethylene, polystyrene, polyvinyl butyral, styrene butadiene, polyacrylates, fumartes, maleates, and methacrylates. The common practice in the coatings industry is to limit the category to the former group. In the latter group, those with application in painting metal surfaces will be discussed at the end of this section. The long carbon to carbon chains common to vinyl resins make them thermoplastic, with good abrasion resistance and durability. They are chemically resistant, and, generally, the longer the chain, the stronger and the less soluble the polymer, and the higher its viscosity. This flexibility in formulation means that vinyls can be truly dissolved in organic solvents as a solvent-borne coating or dispersed as in a high solids. They also can be formulated as waterbornes. Vinyls tend to chalk less than epoxies when exposed to sunlight, but are generally inferior to epoxies in abrasion and solvent resistance.[2,5]

Vinyls can be used anywhere that is not continually exposed to water. Vinyl paints dry by evaporation and are little affected by temperature. They can be formulated for use either as primers or topcoats.

For the purpose of this discussion, vinyls are categorized as follows:

- Vinyl chloride, vinylidene chloride polymers, and copolymers
- Vinyl acetate polymers and copolymers
- Specialty vinyls

Those applicable for painting metal surfaces as in ships are emphasized.

5.1.6.1 Vinyl Chloride ($H_2C = CHCl$) and Vinylidene Chloride ($H_2C = CCl_2$)

The vinyl chlorides and vinylidene chloride polymers and copolymers will be discussed together because the chlorine atoms common to both not only add to the mutual ease of polymerization, toughness, and nonflammability, but they also share the tendency to be unstable with heat 110 to 121°C (230 to 250°F) or under ultraviolet light, splitting out hydrochloric acid (HCl) and developing unwanted color. This problem can be dealt with by using certain pigments, sunscreen agents, or heat stabilizers that will reflect or absorb harmful rays. Vinyl chloride resins can be stabilized by a number of additives:

- Lead pigment
- Organic-tin compounds, tin mercaptides
- Barium-cadmium-zinc complexes (not free ions)
- Calcium-zinc complexes (not free ions)

Vinyl chloride resin stability can also be controlled by secondary stabilizers, usually epoxides that are used in conjunction with the additives mentioned previously.

Normally, selecting a stabilizer for a coating is relatively easy because films are thin and any initial traces of HCl can evaporate. Also, the coating contains enough pigment to protect the resin from light. Application on metal surfaces containing iron or zinc ions, even if just from a surface preparation process, causes a potential problem because these ions themselves can contribute to accelerated thermal discoloration and actual decomposition of coatings. This problem can be

alleviated by chemical surface preparation, restricting pigment selection to those not containing iron or zinc salts, using primers, or adding heat stabilizers, such as an epoxy-tin combination or ureaformaldehyde resins to the coating itself.[2,4]

Polymers of vinyl chloride can be formulated as water- or solvent-borne, or as high solids. Each will be discussed separately:

- Waterborne Vinyl Chloride and Vinylidene Chloride Coatings: These are of extremely fine particle size (0.1 to 0.2 microns). The vinyl chloride polymers can be modified with vinyl acetate, acrylic, or maleic acid esters and plasticizers. Heat and light stabilizers often are added. Copolymers of vinylidene chloride may be modified with acrylonitrile, acrylic esters, or vinyl chloride.

- Solvent-Borne Vinyl Chloride-Based Coatings: The solvents that are usually required are relatively strong, polar solvents - ketones, nitroparrafins, high purity esters, and some chlorinated hydrocarbons. Aromatic hydrocarbons are used as diluents. Vinyl chloride polymers are compatible with alkyds and with some thermosetting resins, such as urea-formaldehyde.

  There is a wide choice of pigments in solvent-borne vinyl chloride polymers. The only restriction, already discussed, is the use of iron or zinc salts, which can affect heat stability and performance on exterior surfaces.

  There are many metal coating applications of vinyl chloride copolymers containing vinyl chloride maleic acid, and vinyl acetate because of the improved adhesion to metal due to the presence of carboxyl groups (from maleic acid).

  Top coats are usually cured at ambient temperatures, primarily to volatize solvents, assure good bonding to the primer and to bring up the gloss. If the top coats are to be subjected to temperatures above 121°C (250°F) during use, then a heat stabilizer, such as an epoxy-tin complex, would be necessary. Pigmented top coats, with baked finish, offer excellent properties of toughness, durability, and chemical resistance. They are useful for coating machinery, appliances, and metal items of all types.

- High Solids Vinyl Chloride-Based Coatings: Vinyl chlorides of high molecular weight are often formulated as high solids. These high solids coatings, often

called dispersion coatings, differ from solution coatings in that the polymer is not dissolved but rather is suspended in a liquid medium (high solids are called organosols), when the suspending medium, which influences viscosity, is a mixture of polar (dispersant) and nonpolar liquids (diluents). Solvents commonly used in vinyl organosols are ketones, preferably diisobutyl ketone, esters, and glycol ethers. Common diluents, which are really nonsolvents, are usually aromatic or aliphatic hydrocarbons. When a liquid plasticizer (basically nonvolatile) is the suspending liquid, these high solid dispersions are called plastisols.

The same limitations concerning the use of iron and zinc as pigments or additives apply to vinyl chloride high solids formulations of both types. The use of heat stabilizers, especially tin mercaptide and epoxy stabilizer (possibly with barium-cadmium-zinc complexes), are beneficial. Otherwise, pigments and extenders may be used as desired, taking note of their influence on viscosity.

Unmodified vinyl organosols do not adhere strongly to metals, even with high temperature cure, but they do adhere well to cured solvent-borne vinyl primers. Consequently, a two-coat system is effective and is used where toughness, abrasion, and chemical resistance are required.

Plastisols also do not adhere well to smooth, impervious surfaces. Primers may be used, but because of the solvent action of plasticizers, there may be some migration of topcoat into the primer. This problem can be overcome by using thermosetting primers that are usually a combination of vinyl and heat-reactive resins. Plastisols are used on metal parts, and are especially useful where a tough, flexible wear layer is necessary.

High solid vinyls modified with carboxyl groups have recently been introduced. They have better adhesion and cross-linking properties than non-modified vinyls.

5.1.6.2 Vinyl Acetate-Based Polymers and Copolymers

Polyvinyl acetate ($CH_3COOCH=CH_2$) polymers are normally formulated as latexes for use as adhesives, paper coatings, and paints. Some are formulated as powder coats with specialty applications as industrial coatings. Their use on metals is limited because the acetate side group, being bulkier than the

chloride group in vinyl chlorides, keeps the chains from packing; therefore, the resin is less strong and more easily penetrated by solvents and moisture. This also tends to make them soften at lower temperatures. Conversely, by the absence of the chloride group, they are more heat and light stable. They are permanently thermoplastic and heat sealable.

5.1.6.3 Miscellaneous Vinyl Resins with Applications in Painting Metal Surfaces

Polyvinyl butyral resins, considered a derivative of vinyl acetate, usually has application in painting metal surfaces as a wash primer or as a metal conditioner used to inhibit corrosion. This is considered surface preparation and is not covered by this study. A new zinc-rich primer based on polyvinyl butyral has been developed. The polyvinyl butyral is part of the binder and displays the anticorrosive properties of the wash primer.

5.1.7 CHLORINATED RUBBER

VOC's associated with chlorinated rubber paints are xylol and mineral spirits, and comprise from 44 to 68 volume percent of these paints. One liter (0.26 gallon) of these paints would contain 0.40-0.61 kg (0.87 to 1.3 pounds) of VOC.

The marine industry has accepted chlorinated rubber coatings as good performing, general purpose coatings. They offer outstanding resistance to water and corrosive chemicals. Chlorinated rubber coatings are applied to ships' superstructure, topside equipment, and hull.

Chlorinated rubber paint can be applied by airless spray resulting in a high build which protects against corrosion with few coats. These coatings can be applied at almost any temperature with minimal surface preparation. This makes them ideal for ships built or serviced during the winter time. Chlorinated rubber paints dry by evaporation of the solvents so the ambient temperature is not too important.

Chlorinated rubber coatings are not high performance coatings although they are superior to conventional alkyds. The general use has been primarily on external parts of the ship, except machinery, due to their resistance to water. They are used as primers, intermediate, and top coats on decks and hulls.

5.1.8 INORGANIC ZINC COATINGS

VOC's used in solvent-borne inorganic zinc paints are ethyl alcohol, isopropyl alcohol, and Cellosolve™. The VOC content

ranges from 21 to 52 volume percent. Each liter (0.26 gallon) of this paint would contain 0.17-0.41 kg (0.37 to 0.90 pounds) of VOC.

These coatings offer excellent protection against corrosion. The zinc reacts with oxygen to give zinc hydroxide which further reacts with carbon dioxide to yield a film of zinc carbonate. Zinc carbonate is an insoluble film that retards further corrosion so that the metallic zinc is not depleted too rapidly, thereby lengthening the life of the primer.

Inorganic zinc coatings cannot be attacked by near neutral solvents or chemicals. They are therefore primarily used for the protection of tanks and other areas requiring good resistance to corrosion and mechanical stress.

Waterborne inorganic zinc coatings can be applied as long as the temperatures are above freezing. Below freezing temperatures, alcohol is frequently added as an antifreeze which adds to VOC emissions.

Inorganic zincs can be applied by all conventional methods.

5.1.9 ANTIFOULING COATINGS

VOC's used in antifouling paints are xylol and methyl isobutyl ketone, and range in composition from 39 to 60 volume percent of the paint. One liter (0.26 gallon) of this paint would contain 0.35-0.54 kg (0.77 to 1.2 pounds) of VOC.

Antifouling coatings consist of antifouling agents bound into surface coatings to control marine growth on a ship's bottom. The coatings are formulated to release active compounds into the water to kill or repel fouling organisms as they develop.

Three types of coating systems are available as follows:

- Single Coat

  This is the most common antifouling coating. The basic principle is the timed release of antifouling agents at a rate which will kill marine growth. Timed release is important so that the coating does not lose its effectiveness too soon.

- High Build

  This system is based on periodic removal of old antifouling paint to expose fresh new layers. When the outer layer of antifouling paint is exhausted, the layer is mechanically scrubbed off. This results in fresh

toxin being released from the newly exposed paint layer. There is a limit as to how often this can be done, which varies with each paint formulation. There are systems available that do not require repainting for up to five years under certain operating conditions.

- Self-Polishing

  This system relies on self-polishing properties whereby the coating gradually wears away by friction of the ship through water. The hull actually becomes smoother resulting in fuel savings. As the coating wears away, fresh toxins are released at a constant rate between drydockings.

  Since the antifouling coating is worn away, there are no built-up layers of paint that must be removed prior to recoating.

  Antifouling paint may be applied by all conventional methods--airless spray, air spray, roller, and brush. They are easily thinned with xylene. The primary method of curing is by evaporation of solvent at ambient temperatures.

5.2 THE ROLE OF VOC IN PAINT

Paint consists of a binder, pigments, solvent and special purpose additives. The binder determines the film formation characteristics and the performance of the paint coating. In its liquid form the binder is usually diluted by the solvent to prepare the paint for application. The pigment imparts decorative value, including color, gloss, light fastness, etc. Paint solvents include any volatile liquid that acts as the vehicle for uniformly dispersing paint solids--organic compounds, water, or some combination of the two.

The nature and quantity of solvent in paint controls the consistency to make the paint suitable for application. The choice of solvent influences viscosity, setting rate, drying time, and pigment dispersion. The degree of dispersion affects film flexibility, hardness, strength, and weatherability. This is even though solvents evaporate during drying and do not become part of the paint film.

Aside from their use in paints, solvents also are used for cleaning painting equipment. Because of its expense the solvents are usually recirculated and reused until they can no longer be used for cleaning. At this point they are usually drummed for disposal. The quantities of VOC emitted from this

source will vary depending on cleaning practices. Some yards, for example, let the solvents evaporate as they are used without attempting any recycle.

Many paints used in the marine industry are also common industrial paints. A general description of solvents commonly used in the paints is shown in Table 5-3.

Table 5-3

Description of Organic Solvents Used in Marine Paints[2]

Classification	General Information	Specific Compounds
Paraffins (Alkanes)	These exist in two forms: normal paraffins and isoparaffins. Low odor. As molecular weight increases, volatility and solvency decrease.	Heptane Hexane Cyclohexane
Aromatics	Usually based on the unsaturated, six-carbon-ring structure of benzene. High solvency and strong odor.	Benzene, Toluene, Xylene, Ethyl Benzene, Xylol Tetramethyl Benzene
Alcohols	A hydrogen atom of an aliphatic hydrocarbon is replaced by a hydroxyl group. Water soluble. Mild, usually pleasant odor.	Methanol Ethanol Isopropanol Butanol Methyl Isobutyl Carbinol 2-Ethyl Hexanol Octanol Diacetone Alcohol Hexylene Glycol
Esters	These result from the reaction of an alcohol and an organic acid. Most common use in lacquers. Pleasant odor.	Sec-Amyl Acetate Sec-Butyl Acetate Ethyl Acetate n-Butyl Acetate Isopropyl Acetate Cellosolve™ Acetate (Cellulose Acetate) Methyl Amyl Acetate Ethylene Glycol Monoethyl Ether Acetate

Table 5-3

Description of Organic Solvents Used in Marine Paints[2]
(Continued)

Classification	General Information	Specific Compounds
Ketones	These compounds are characterized by the C=O group. Usually bad odor.	Pentoxone Methyl Ethyl Ketone Diisobutyl Ketone Acetone Isophorone Methyl Isobutyl Ketone Ethyl Amyl Ketone 2-Butanone 2-Hexanone
Ether - Alcohols	These contain both an alcohol and an ether group.	Glycol Ether(Butyl Cellosolve") Dichlor Isopropyl Ether Ethyl Ether Diacetone Ether Carbitol Ethylene Glycol Monoethyl Ether Allyl Glycidyl Ether Ethylene Glycol Monobutyl Ether Butyl Glycidyl Ether Phenyl Glycidyl Ether Xylenol Glycidyl Ether Cresyl Glycidyl Ether
Substituted Hydro-carbons	These include compounds of the type containing hydro-carbons with attached nitro, amine, chloro and sulfide groups.	Monochlorobenzene Dichlorobenzene Nitromethane Nitrobenzene Carbondisulfide Urea Cresylic Acid Methyl Ethyl Ketoxime Triethylamine Diethylamine Diethylamino Ethanol Chloroform Carbon Tetrachloride Chloroethene Trichloroethylene Perchloroethylene

Table 5-4 shows the most common solvents associated with a particular type of marine paint.

Solvent-borne coatings, by convention, refer to coatings formulated with organic solvents as the dispersing vehicle. Generally, several solvents are used in combination. Solvents are primarily straight chain or aromatic hydrocarbons. Despite their high cost, oxygenated solvents are also used because they are stronger solvents.

There are two basic types of solvent-borne coatings. They are lacquers (thermoplastic) and enamels (thermosetting). Lacquers contain thermoplastic resins that cure by solvent loss. The paint film is held together physically rather than by chemical forces. The binder in the dry film is chemically the same as it was in the paint can. Enamels, on the other hand, undergo a chemical reaction upon curing resulting in cross-linking of the paint molecules. There are two mechanisms of chemical reaction. One is by air oxidation, the other is by chemical reaction of the binder without air taking part. Some examples of each are listed below:

Thermoplastic, Physical drying: Chlorinated rubber, other chlorinated resins, vinyls, acrylics, and PVA emulsions.

Thermosetting, Chemical drying: Alkyd enamels, epoxies, tar epoxies, polyurethanes, zinc silicates.

The following is a summary of advantages and disadvantages in the use of solvent-borne as compared to waterborne coatings:

- Advantages:
  - Suitable for application by most methods.
  - Most common, therefore, readily available.
  - Technology and equipment already developed and in use.
  - Reliable.
  - Less sensitive to contaminants.
- Disadvantages:
  - Air pollution is caused by emission of solvents.
  - Fire hazard and exposure limitations demand large air exhaust system to keep concentration of solvents low.

Table 5-4

Common Paint-Solvent Systems
for Marine Applications

Paint	Associated VOC (in order of highest use)
Alkyd	Mineral Spirits
Antifouling	Xylol Methyl Isobutyl Ketone
Chlorinated Rubber	Xylol Mineral Spirits
Epoxy (catalyzed)	Xylol n-Butyl Alcohol Naphtha Butyl Alcohol Aromatic Hydrocarbons
Polyurethanes	Cellosolve" Acetate Ethyl Amyl Ketone Methyl n-Butyl Ketone
Inorganic Zinc (organic-solvent based)	Ethyl Alcohol Isopropyl Alcohol Cellosolve"

- A limited quantity of paint can be stored in an area due to safety regulations.

- Higher cost and questionable availability are predicted for solvents in the future.

5.3 WATERBORNE PAINTS

Waterborne paints get their name because water is the major solvent. The paint resin may be dissolved or suspended in the water. Despite their name, organic cosolvents are almost always used to improve wetting, control viscosity, and disperse resin and pigment. Water soluble resins usually contain around 20 percent organic cosolvents. Suspended resins may have less than 5 percent organic cosolvents. These cosolvents are primarily oxygenated solvents (ketones, alcohols, glycol ethers) and amines. Waterborne paints are currently available for resins such as epoxies, acrylics, polyvinyl acetates and inorganic zinc. Both dissolved and suspended resin paints display properties similar to conventional solvent-borne paints. These are weather and chemical resistance, durability, and toughness.

Freezing can be a problem for waterborne paints. Emulsion waterbornes are more of a problem than solubles because the cosolvent content is only about 5 percent and the freezing point of the paint is not significantly reduced. Soluble waterbornes usually are not affected by freezing, whereas emulsions are often destroyed.

Waterbornes may be either thermoplastic or thermosetting. Depending on the particular resin, waterbornes can be applied by brush, roller, and all forms of spray. Table 5-5 compares solids content by type of paint.

Table 5-5

Percent Solids by Type of Paint

Type of Paint	% Solids (by volume)
1. Waterborne	5-35
2. Solvent-borne	
a. Lacquers	15-35
b. Enamels	25-35
3. High Solids	
a. Medium High Solids	45-70
b. High Solids	60-95

There are unique advantages and disadvantages associated with waterborne paints. Due to the conductivity of water, special care must be used when applying electric current to an application process (i.e., electrostatic spray) to make sure all wiring is grounded or insulated. Because water is corrosive, exposed metal surfaces in spray booths have to be protected. Curing of waterborne paints is affected by temperature and humidity. Waterbornes must be properly cured or their resistance to water will be decreased. Waterbornes have definite fire and explosion advantages because of the low organic solvent level.

The following is a summary of advantages and disadvantages to consider when using waterborne as compared to solvent-borne paints:

- Advantages:
  - Less unpleasant odor is experienced.
  - They are non-flammable.
  - Reduced solvent emissions are possible.
  - A cleaner, healthier, less toxic environment is provided for workers.
  - Waterbornes use conventional application techniques.
  - Waterbornes use conventional equipment with ease of conversion and minimal disruption in many cases.
  - Color, impact and corrosion resistance, gloss, and weatherability compare favorably to solvent-borne coatings in many applications.
  - Formulation not primarily dependent on petroleum-based solvents whose availability and cost have an uncertain future.
  - Storage life is good.
  - Although the surface to be painted needs to be clean before application, no revision of surface preparation procedures is usually required.
  - There can be a reduction in air atomizing pressure and agitation for waterbornes over solvent-bornes.
  - Handling costs can be reduced because an 8-hour supply can be stored at a booth without violating fire regulations.

- Waterborne coatings can be applied over solvent-based coatings.

- Disadvantages:

  - Protection from freezing is required for some waterborne coatings.

  - For use with electrostatic or electrodeposition operations the system must be electrically insulated. An alternative is to use intermediate reservoirs that are insulated and isolated.

  - Humidity and temperature are very important as they affect evaporation rate.

  - Wet-on-wet application may not be possible.

  - Metal surface preparation and cleaning are often more critical.

  - Efficiency of waterbornes using airless electrostatic equipment is lower than that of solvent-borne coatings.

  - Due to their generally higher heats of evaporation, longer curing times and higher temperatures, drying times will usually be affected.

  - Air drying is not reliable due to humidity problem.

  - The performance of waterborne paints has not, in general, been satisfactory for marine applications. Anticorrosive coatings are the exception to this.

5.4 TRENDS IN INDUSTRY

5.4.1 THE USE OF TWO-PART REACTIVE PAINTS

Six shipyards supplied estimates of the change that two-part reactive paints have made in their total paint use. Half the shipyards showed an increase in the amount of two-part reactive paints used, while the other half reported no change. Two other shipyards did not have the figures available. The data is shown in Table 5-6.

These paints cure by the reaction of two ingredients, thus the name "reactive." Two-part paints may be mixed just prior to application or they may be mixed in the head of the paint spray gun.

Table 5-6

Two-Part Reactive Paint as Percent of Total Paint Use

Shipyard	Current	Five Years Ago
1	60	30
2	50	0
3	60	45
4	50	50
5	5	5
6	15-20	15-20
7	-	-
8	-	-

The advantages of two-part paints include: higher efficiency of application, less solvent being used, lower shipping cost, possibly fewer coats of paint need be applied, and possibly a reduction of air flow inside the ship or spray booths because of their lower solvent content.

As the paint components polymerize, the molecular weight of the solids in the coating increases. From Table 5-5, it can be seen that high solids paints contain an average of 50 percent more solids than low solids paints, and generate less solvent emissions because of their low solvent content and higher efficiency of application.

5.4.2 THE USE OF WATERBORNES

Four of the eight shipyards visited use waterbornes in some measurable quantity. The highest use was only 5 percent of total paint use. From interviews, it was apparent that either a shipyard uses waterbornes at ≈5 percent of total paints consumed or it uses hardly any. The only waterborne paints reported in use were coal-tar emulsions and inorganic zinc primer. Very little waterborne paint is being marketed for marine use besides these two uses.

Waterborne paints have not gained major acceptance in ship painting because they generally offer no significant performance advantages over commonly used solvent-borne paints and frequently cost more. As noted in Section 4, the shipyards generally do not have the option of selecting the paints they use as this is dictated by the shipowners.

Table 5-7 presents the survey results with regard to the use of waterborne paints.

Table 5-7

Waterborne Paint as Percent of Total Paint Use

Shipyard	Now	Five Years Ago
1	5	0
2	5	0
3	<1	<1
4	0.1	-
5	<1	<1
6	0	0
7	0	0
8	-	-

5.4.3 MARINE PAINTING RESEARCH

Several organizations are currently performing research in the field of marine paint systems. The National Shipbuilding Research Program in conjunction with the Maritime Administration is conducting research that tests currently available commercial paints rather than develop new paint systems. The test program subjects commercial paints to various marine conditions to determine their suitability for use in or on ships.

Project PACE (Performance of Alternate Coatings in the Environment), sponsored by the Steel Structures Painting Council, evaluates the durability of new types of paints, raw materials, and surface preparation methods for structural steel. The program provides information on alternative coating systems designed to prevent corrosion while complying with present and expected legislation covering pollution. Other studies that may be beneficial to marine painting include a project to optimize paint film thickness.

The Naval Ship Research Center of the Navy Department researches paint systems and paint application equipment. The paint system research includes testing and evaluation of new paint formulations as well as reformulations of currently available paint. Antifouling paint currently accounts for 75 percent of the R&D budget, with the remainder of the budget going for anticorrosive paints. Several programs also exist for the development and testing of waterborne paint. Two of these programs are for interior and topside maintenance paints. Early results from these two programs indicate more promise for waterborne paints in marine uses than earlier research.

The primary aim of research undertaken by paint formulating companies used to be substitution of organic solvents by water. However, formulators are now searching for new materials and systems to cope with the problems of energy demand, toxicity,

cost, and odor. The need for better equipment in the application of high solids paints is also being emphasized. Antifoulant coatings research is trying to extend service life beyond 24 months. More frequently, paint formulators are coming out with paints that provide up to 30 months protection. With antifoulants comprising the major portion of maintenance painting, VOC from repair facilities can be expected to decrease in the future based on life-cycle emissions. Several companies have also come out with computer generated paint maintenance programs. A custom-made hull paint maintenance program for individual ships has demonstrated a reduction in maintenance painting. New formulations also include 100 percent solids materials that are a solvent-free coal tar epoxy or a solvent-free pure epoxy. Besides decreasing VOC emissions, solvent-free materials can be used without the danger of explosion.

SECTION 6

VOC EMISSION CONTROL TECHNOLOGIES

6.1 INTRODUCTION

There are three possible approaches toward reducing the amount of VOC emissions from a painting operation:

1) Modify the paint formulation either to contain less solvent or to have a longer service life

2) Capture the emissions before they are released to the environment and then either reclaim or destroy them

3) Improve the paint application technology in order to increase the paint transfer efficiency and reduce the amount of paint used.

These approaches are not mutually exclusive and any combination of the three is worth considering. Each approach has constraints which may make individual technologies inapplicable for ship painting. For example, powder coatings virtually eliminate VOC but because of high curing temperatures, among other reasons, they cannot be utilized for hull painting.

This section will explain how each of the three approaches can be applied to the ship painting industry, the associated constraints, and the related trends in industry.

6.2 MODIFICATION OF PAINT FORMULATIONS

As detailed in Section 5, organic solvents (VOC) play a vital role in the formulation, application, and curing of paints and except in a few instances cannot be eliminated entirely from the formulation. Table 6-1 shows the VOC volume percent of various paint types used in ship painting. It is clear from the table that the amount of VOC in paints is both variable and substantial ranging from 20 to 82 volume percent.

In recent years there has been significant progress in reducing the VOC content of paints which is attributable to environmental and economical factors. Environmental regulations in industries

Table 6-1

Solvent Proportions by Type of Paint

Type of Paint	Volume Percent Solvent
Acrylic	52-68
Alkyd	40-65
Antifouling	39-60
Chlorinated Rubber	44-68
Epoxy	20-79
Inorganic Zinc (organic solvent)	21-52
Inorganic Zinc (water solvent)	23-43
Polyurethane	45-56
Vinyl	53-82

other than ship painting have forced paint formulators to develop low solvent paints to meet the demands of their customers. Aside from regulatory compliance, economical benefits were also observed and most of these benefits have been directly transferable to marine coatings.

Economic benefits accrue partially because, as discussed earlier, solvents evaporate from paints totally and do not become part of the coating. Less solvent in the paint leads to direct savings because less solvent is evaporated away. Low solvent paints may be applied in thicker layers which means that fewer layers are required to reach a specified coating thickness. Some low solvent coatings, for example, can be applied in one application instead of four separate applications, for a 75 percent reduction in labor costs.

Another effective modification to paint formulations that results in reduced life-cycle VOC emissions is the use of high-performance coatings. Painting a ship every year will cause twice the emissions associated with a ship painted every 2 years. For ship owners the overpowering reason for specifying a high performance coating is cost rather than the environment. When out-of-service time is considered, a day in drydock can cost anywhere between $5000 and $100,000. While all high-performance coatings have substantially higher first costs than conventional systems, these costs are more than offset by the coating's effectiveness and durability and the resultant reduction in out-of-service time.

Shipyards visited as part of this study indicated increased use of high-solids coatings and increased acceptance of waterborne coatings over the past 5 years. Utilization of high-performance coatings also is rising rapidly. All shipyards consulted expressed a preference for state-of-the-art paints over those used in the past (many of which are still required for military applications). This trend has not been directly due to environmental regulations but has developed primarily because of the costs associated with protecting a ship's hull from corrosion and control of biotic fouling which has become critical with the high costs of fuel. The effects of this trend on the amount of VOC emissions from ship painting operations are unknown due to a lack of data; however, a net reduction in emissions would be expected.

6.3 CAPTURE TECHNOLOGIES

Paint booths or hoods are commonly used throughout the metal finishing industry to contain and remove emissions from painting operations.[2] Exhaust from these systems can be ducted to an incinerator where the VOC are destroyed or to a carbon absorption unit for removal before being released to the environment.

The nature of ship maintenance work, however, would make any kind of enclosure system very expensive from both a capital investment and energy cost viewpoint. Enclosures would have to be designed specifically for each facility and would be some of the largest structures in the world. Air flows would be large and the VOC content of the air would be very low requiring the energy consumption for incineration to be very high. Such a system would be clearly unreasonable.

An alternative system would be to have a small traveling enclosure just large enough to cover the immediate area being painted. As it is likely that several of these hoods would be operating on a ship at a given time, a maze of exhaust hoses with potentially explosive gas mixtures would develop. The safety problems would be complex and would include the problem of flashbacks from the incinerator to the painter through the exhaust hose. The shape of the hull would dictate what kind of support mechanism could be used for the hood and may make support infeasible. If it was feasible to design such a system it would probably collect only a portion of the VOC being emitted. Some solvent would evaporate from the surface while the paint cures after the hood has left the area.

No references were found indicating that capture and destroy or recovery systems for VOC emission control are being used or considered by the ship painting industry.

6.4 EMISSION REDUCTIONS BY IMPROVING APPLICATION TECHNOLOGIES

6.4.1 OPTIONS FOR APPLYING PAINTS

The choice of a particular paint application process reflects consideration of: the material to be coated; the product configuration; the desired coating properties; the extent of production; environmental considerations; and other factors. When considering the painting of ships, processes such as flow coating, dip coating, electrodeposition, and barrel coating are easily eliminated in spite of their high transfer efficiencies because they are physically infeasible. Conventional brush and roller application is far too labor-intensive for the bulk of ship painting and is used only where necessary. If the proper technology were developed, roller coating could become an attractive alternative application technology for the large essentially flat surfaces present on a ship because it has nearly a 100 percent transfer efficiency. Powder coating by any application process is eliminated because of the properties of powders which, among other problems, require a high-temperature cure. Ship painters are thus left with spray painting as the only practicable application technology available to them. As spray painting can be extremely wasteful of paint and accordingly generate very high VOC emission rates, it is useful

to understand the technology in order to know its limitations and potentials. Air and airless spray, and electrostatic versions of both are available to ship painters and are described in the following section.

6.4.2 SPRAY PAINTING TECHNOLOGIES

Spray painting is by far the most common application method and can be used with almost all varieties of paint to coat most types of materials.

The main components of a typical spray painting system are a pumping system, an atomizing system, and a spray gun.

Spray painting is accomplished by driving finely divided particles onto the surface being coated. Varieties of spray application include air spray, airless spray, and electrostatic spray.

Air spraying utilizes high pressure air to atomize paint and to drive it to the surface being coated. An air atomized sprayer may be either hand-held or automatic although ship painting is not very amenable to automatic systems. Hand-held sprayers are very useful for painting unusual contours and complicated shapes because of their portability. The greatest strength of hand-operated spray painting is its versatility. Many different operating conditions can be accommodated by skillful sprayers and careful solvent blending. At this writing, approximately 20 to 30 percent of the paint used in shipbuilding yards is applied by air spraying.

Compressed air is used in air spraying as the driving force. The compressed air flow and the pressure for the paint and atomizing lines are regulated. The fluid lines connect to the paint pot which may supply one or several guns through the paint line. The atomizing air line connects directly between the pressure regulator and the spray gun (see Figure 6-1). The spray gun may be pressure or suction fed. The pressure gun is used to paint large areas rapidly. The suction-fed gun forces high velocity air across the nozzle creating a vacuum in the feed line which draws the paint up into the nozzle to be atomized. Both pressure fed and suction fed systems are commonly used in shipyards.

Air spraying produces large quantities of overspray caused by turbulence of the high velocity air impacting and rebounding from the surface and carrying paint with it. This wasted paint is referred to as "overspray." Air spraying has only a 40 to 60 percent transfer efficiency because of the paint loss due to overspray. The skill of the painter has a significant impact on the transfer efficiency as angle of spray and distance from gun

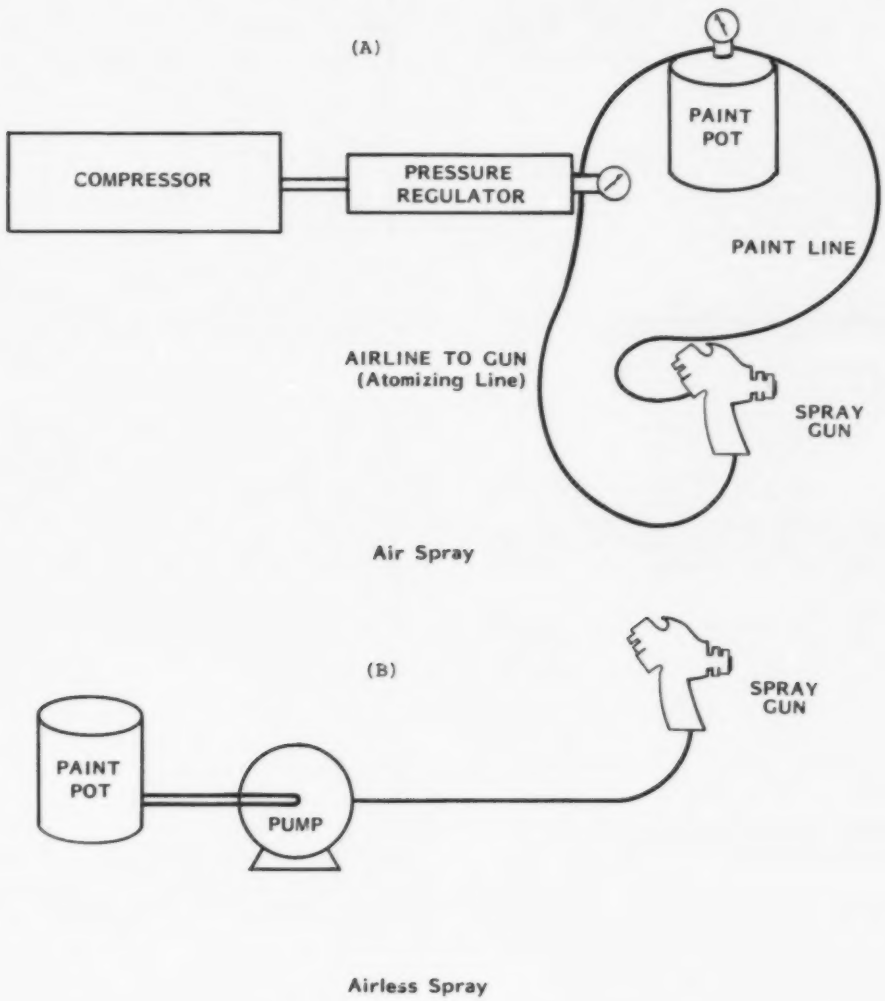

Figure 6-1. Paint Spraying Systems

to object, both of which effect efficiency, are at the control of the operator.

Airless spraying is a method of spray application that does not directly use compressed air to atomize the paint or other coating material. Hydraulic pressure is used to atomize the fluid by pumping it at high pressure 35 to 316 kg/sq-cm (500 to 4500 psi)) through a small orifice in the spray nozzle. As the fluid is released at these high pressures, it is separated into small droplets resulting in a very fine spray. Water, for example, is hydraulically atomized by the fine spray adjustment on a garden hose nozzle; however, it is accomplished with low pressure because of the low viscosity of water. Paint and other coating materials have a higher viscosity and therefore require higher pressures. The fluid is discharged from a small nozzle orifice at such a high velocity that the material tears itself apart. Sufficient momentum remains to carry the minute particles to the surface.

Airless spraying can accommodate much more viscous paints than air spray, which has aided the acceptance of low solvent paints by industry. Airless is used widely to apply zinc primers and other highly pigmented paints and is especially useful for large objects. There has been a definite trend in the ship painting industry toward higher utilization of airless spray.

Since air is not used to atomize the paint, the term "airless" is used to describe this method. Turbulence and blow back are greatly diminished due to the absence of air. Consequently, higher paint transfer efficiencies of up to 70 percent are realized.

Air pressure is required to operate an air motor which powers a reciprocating airless fluid pump. The pump develops fluid pressures at a given ratio depending on the size of the air motor piston and the effective area of the fluid piston. For example, a pump rated at 25:1 develops fluid pressure 25 times the air pressure applied to the air motor. For 7 kg/sq-cm (100 psi)air pressure, 176 kg/sq-cm (2500 psi) fluid pressure results.

Another option available for spray painting which can reduce VOC emissions is the use of hot spray. Very viscous paints are made pumpable by heating rather than thinning with solvents. In hot spray, the paint solution is heated, usually to an operating temperature of 38 to 66°C (100 to 150°F). Hot airless spray reduces the amount of overspray that contaminates a work area and wastes paint. Because the viscosity of the solution is lowered by heating, much higher solids content is achievable with hot spraying, thus lessening the amount of solvent evaporated into the atmosphere. Higher solids painting also permits a thicker film buildup per pass of the spray gun without risk of runs or sags in the coating.

Electrostatic spray painting is accomplished by placing a high voltage electrical charge on each particle of paint. The object to be coated is an electrically conductive ground. Some of the paint particles that would normally miss the work will now be attracted to the edges and back side of the work. This effect is commonly referred to as the "wrap around" effect and represents the principle advantage of electrostatic spraying. This effect offers little benefit in the painting of ships hulls.

The material can be atomized in one of two ways: The first is to use the electrostatic force created by high voltage differential between a paint dispenser and the grounded work. This force tears the material apart effecting atomization and deposits the material on the object to be coated. No air or hydraulic force is used. This method is sometimes referred to as "true electrostatic painting." The material is fed to a rotating disc or bell. A set speed will cause the material to flow by centrifugal force to the edge, but not disperse. The disc or bell is charged to 120,000 volts D.C. negative (excess of electrons). As the object to be coated passes by the rotating disc or bell, the material is pulled off by a current exchange between the emitter and the product and is attracted to the work. This type of electrostatic finishing is used by most major appliance manufacturers because of the high required production volume and uniformity of the parts to be coated. These systems are generally not purchased but leased from equipment manufacturers.

The second method is to atomize the material first, using air or hydraulics as the force. The high voltage charge is then induced into the spray pattern and in turn adds an electrostatic charge to the atomized material particles. The attraction between the atomized particles and the work is strong enough to bend the overspray around the product depositing most of the material on the back side of the work.

The principles of equipment operation and material supply are the same as for standard airless or conventional equipment. However, the appearance of the equipment is somewhat different as it is constructed of materials designed to carry the necessary high voltage.

The application of electrostatic spraying in the shipbuilding industry has not been implemented for a variety of reasons:

- Electrostatic spraying's wrap-around effect offers no advantage in the application of paints to the large, relatively flat surfaces encountered in ship painting. In addition, the required thickness of the coating is difficult to attain because the conductivity of the surface is diminished as the coating thickness increases.

- Extraneous forces, such as air movement opposing the field force, must be avoided in the use of electrostatic spraying. The necessity of outdoor spraying in the painting of ships would limit application to calm days.

- The addition of electrostatic spraying equipment to the airless equipment currently in use would add approximately $2500 to the investment cost of each spray unit.

- A power pack required for electrostatic equipment weighs up to 200 pounds. The addition of this equipment would severely limit the portability of spraying equipment.

- The use of electrostatic equipment requires special safety considerations to prevent static discharges. These precautions would be particularly difficult with a portable unit.

- The conductivity of paint formulations is of critical importance in the use of electrostatic equipment. Many highly conductive paints cannot be applied with this method.

Electrostatic application of paints to aircraft has recently proven successful.[12] This method is of utility in that industry because the surfaces being coated are nearly all contoured and only thin coatings are required. It appears that there is little likelihood that shipbuilders will be attracted to electrostatic application technologies.

6.4.3 NEW TECHNOLOGY

Technologies do exist which could greatly reduce or eliminate VOC emissions during ship painting but considerable research would be required to make the technologies applicable to ship painting and, in addition, to develop the paints necessary for the application. The technologies would be UV or electron-beam curing of paints which use little or no VOC as solvents. There is no indication that such technologies are even being considered for this industry because of the many technical questions which must be answered.

One technology having some potential for reducing VOC emissions was discovered and is unique to the ship painting industry. At Norfolk Shipbuilding and Drydock Company a machine known as a Docknight™ is used to paint ships at a capacity rating of an acre an hour. By keeping the spray perpendicular to the surface and minimizing the number of paint overlaps it is expected that the amount of paint required per ship would be reduced with concurrent reductions in VOC emissions. No data are available to quantify the savings. A technical description of the device follows.[3]

The Docknight™ is a welded traveling platform on which is mounted one 781 kg-cal/min (73 HP) diesel engine for driving hydraulic pumps, one 2890 kg-cal/min (270 HP) engine connected to a triplex pump with an output of 9.5 liters/sec (150 GPM) at 188 kg/sq-cm (2680 psi), an operator's cabin, three hydraulically operated paint pumps, and a base boom including the electronics and hydraulics necessary to operate and automate the system. Connected to the base is a working boom with an attached work cage. The Docknight™, originally designed as a waterblasting system, was custom built to NORSHIPCO's specifications to include spray painting capability.

The system has a vertical working range of 30 m (98 ft) from the lowest point to the extreme height. Its range can accommodate ships with a beam of 35.2 m (116 ft) to those with a beam of 44 m (144 ft). A lesser range is achievable with smaller ships.

On the end of the working boom is a wheel-activated sensor that guides the working boom automatically to follow the contour of the vessel's hull when the system is in its automatic mode. In addition, there is a push-button indexing system that moves the working boom up or down in increments of 1.1 m (3.6 ft) when in the waterblasting cycle and 1.8 m (5.9 ft) when in the painting cycle. The speed of travel is also adjustable in known increments. The speed of travel is an essential element in determining the mil thickness in the painting process.

The weight of the Docknight™ is 26 metric tons (23.6 short tons) and it is supported on a rail by four wheels. Each wheel is driven by an infinitely variable hydraulic motor. The Docknight™ position is held horizontally on the top rail by guide rollers that run on either side of the vertical face of the rail.

In order to withstand the horizontal forces generated at the lower extreme of the base boom, particularly when the base boom and working arms are fully extended and perpendicular to the side of the dock, the lower column roller is designed to coincide with the safety deck in the drydock.

Four people are required to operate the Docknight™ in the painting mode; one operator, one operating engineer, and two paint handlers. Although the system was designed to pump paint from 208 liter (55 gallon) paint drums, the current procedure employs the use of an open 208 liter (55 gallon) drum which is manually replenished by two paint handlers using 19 liter (5 gallon) pails.

It must be pointed out that this system was designed specifically for use at NORSHIPCO and the floating drydock was modified substantially to accept the Docknight™. The system is not adaptable to many drydocks because of the structure of the docks. As would be expected, the system is quite expensive with

NORSHIPCO's unit costing $1.5 million excluding modifications to the drydock.

The impetus for installing the Docknight™ system at NORSHIPCO was to speed up ship painting in order to decrease turnaround time making the shipyard more attractive to potential customers. While a decrease in paint consumption may have been anticipated, any environmental benefits are welcome but incidental to the primary driving force which is economics. The Docknight™ has been modified to recirculate cleaning solvents, which serves the double function of reducing operating costs by reclaiming solvent and also reducing VOC emissions.

SECTION 7

ESTIMATION OF NATIONAL VOC EMISSIONS FROM MAJOR SHIPYARD PAINTING

Many factors contribute to making an accurate determination of the quantities of VOC being emitted from ship painting operations a very difficult task. Marine paints, for example, are also used to paint oil derricks and other structures exposed to seawater and records for these alternative uses either do not exist or are not readily available. Alternatively, some paints with general industry use are also used in ship painting and records of end uses are not maintained by paint formulators. Additionally, some ships supply their own paint to drydocks from foreign sources. Even if total gallonage records were available, each type of paint has its own solvent associated with it at varying volume percents. Because of these problems and others, it was decided to make several estimates based on independent approaches. By using the approaches described below, a range of VOC emissions was developed. All values were well within one order of magnitude, indicating that a reasonable degree of confidence is associated with them.

The first approach was to utilize the data obtained during the visits to shipyards to arrive at an estimate of the total VOC emission from painting of ships based on employment and paint consumption. Table 7-1 presents a summary of paint use and employment[9] data for the shipyards visited.

Shipyards were divided into three categories for analysis because the significance of the painting operation in relation to the total work load depends on the nature of the shipyard. These categories are:

1. Primarily Construction
2. Construction and Repair
3. Repair Only

The ratio of paint use to employment was determined in each case for which data was available. The expected value of this ratio was found for shipyards falling into each of the three categories listed above. The expected value of annual paint

Table 7-1

Paint Use and Employment
at Shipyards Visited

Shipyard	Primary Current Function	Paint Use l/yr	(Gal/Yr)	Employment		l/man/yr	(Gal/Man/Yr)
Norshipco (Berkley)	Construction/ Repair	488,091	(128,954)	3,500	(79)*	139.45	(36.844)
		306,150	(80,885)	2,500	(78)	122.46	(32.354)
		351,854	(92,960)		(76)		
Avondale (Main Yard)	Construction/ Repair		N/A	N/A			
Todd (Galveston)	Repair	225,208	(59,500)	600		375.35	(99.167)
Jacksonville	Repair	595,358	(157,294)	2,200	(79)	270.62	(71.497)
		484,946	(128,123)	2,305	(78)	210.39	(55.585)
		566,895	(149,774)	2,280	(77)	248.64	(65.690)
Newport News	Construction	1,854,650	(490,000)	22,400	(79)	82.80	(21.875)
		1,816,800	(480,000)	25,000	(78)	72.67	(19.20)
Lockheed	Construction/ Repair		N/A	1,700			
Todd (Alameda)	Repair	188,115	(49,700)	400	(77)	470.29	(124.25)
NASSCO (San Diego)	Construction	642,614	(169,779)	5,453	(78)	117.83	(31.13)
		537,655	(142,049)	6,356	(79)	84.59	(22.349)

*Year

use per employee, with 90 percent confidence limits, is shown in Table 7-2. Because of the small sample sizes involved, the confidence limits were determined using the t-distribution with degrees of freedom equal to one minus the sample size. The assumption that the data represents a random sample drawn from a near-normal population is involved.

Employment figures for all major shipyards are available for a single year (1979)[9]. Total major shipyard employment for that year was approximately 224,600. The number of shipyards and total employment by category are also shown in Table 7-2.

VOC emissions per gallon of paint are a function of the paint type. Data on marine coating sales and resultant emissions by generic paint type are available for the State of California, 1976.[11]

It is reasonable to assume that the distribution of national marine coating sales by generic type closely resembles the distribution determined during this California survey (although our visits have indicated a continuous shift to higher solid-content paints since 1976). Therefore, the weighted average of VOC emission per gallon of paint obtained by the CARB study, .434 kg/liter (3.62 lbs/gal) was used in this approach.

Estimated annual emissions, based on this analysis using data obtained during shipyard visits, are shown in Table 7-2. For a 250 day year the sum of emissions from all shipyard categories is shown to be 70.4 $\pm$ 24.6 metric tons/day (77.6 $\pm$ 27.1 short tons/day) (90% confidence limits).

This estimate agrees very well with the estimate published[1] in 1978 by Booz, Allen, & Hamilton Inc. of 40.8 to 81.6 metric tons (45 to 90 short tons) VOC emitted per day by ship painting operations nationwide. This was based on 1977 data and a 250 day year.

The State of California Air Resources Board (CARB) also published a report in 1978 based primarily on 1976 data which estimated that 13 major California shipyards emitted 9.5 metric tons (10.5 short tons) per day of VOC. Only nine of these yards are actually classified Code A, but assuming all of them were and extrapolating the data to the total 76 code A shipyards yields a national VOC emission estimate of 55.7 metric tons (61.4 short tons) per day.

The National Paint & Coatings Association (NPCA) supplied an estimate of sales of coatings for marine applications of 35.2×10^6 liters (9.3×10^6 gallons) in 1977. This volume is subject to the limitations discussed in the introduction to

Table 7-2

Estimated VOC Emissions from Painting at Major Shipyards
(90 Percent Confidence Limits)

Category	Expected Value of Paint Use per Employee Liter/Yr/Emp	(Gal/Yr/Emp)	No. of Major Yards	Total Employment (1979)	Expected VOC Emissions Metric Tons/Yr	(Short Ton/Yr)
Construction	89.48 ± 23.09	(23.64 + 6.10)	5	38,200	1482.84 ± 382.66	(1,634.52 + 421.8)
Repair and Construction	130.96 ± 53.63	(34.60 + 14.17)	45	117,160	6656.39 ± 2726.05	(7,337.3 + 3,004.9)
Repair	315.03 ± 101.21	(83.23 + 26.74)	26	69,240	9462.73 ± 3040.21	(10,430.7 + 3,351.2)
TOTAL			76	224,600	17601.95 ± 6148.91	(19,402.5 + 6,777.9)

this section but by itself translates into an emission rate of 59 metric tons (65.1 short tons) per day ± 25 percent to account for the range of solvent volume percent in the various paints for a 250 day year. Solvents used for cleaning and thinning are not included in this figure.

An individual paint formulator estimated that the entire U.S. market for antifoulant paints was 1,892,500 liters (500,000 gallons) per year ±20 percent. Using data from the CARB report[11] and extrapolating it to the entire U.S. population of major shipyards yields a daily emission rate of 28.4 metric tons (31.3 short tons) of VOC ± 20 percent. This is based on a ratio of total VOC emissions from all sources for every gallon of antifouling paint applied. There are obvious problems with this approach and it should be considered the weakest of those utilized.

The results of all five estimation approaches are summarized in Table 7-3. Although no single highly reliable number was developed, the reasonable agreement of the various estimates yields a range that can be confidently relied upon as a characterization of the extent of the VOC emission problem from U.S. ship painting operations.

Table 7-3

Summary of VOC Emission Estimates

Metric Ton VOC Emitted per Day (short tons)

250 days/year	365 days/year
1. 70.4 ± 24.6 (77.6 ± 27.1)	1. 48.2 ± 16.8 (53.2 ± 18.6)
2. 40.8 to 81.6 (45 to 90)	2. 27.9 to 55.9 (30.8 to 61.6)
3. 55.7 (61.4)	3. 38.15 (42.0)
4. 59.0 ± 14.8 (65.1 ± 16.3)	4. 40.4 ± 10.1 (44.6 ± 11.2)
5. 28.4 ± 5.7 (31.3 ± 6.3)	5. 19.5 ± 3.9 (21.4 ± 4.3)

Basis of Approach

1. Employment and paint consumption based on site visits
2. Booze, Allen, & Hamilton report[1]
3. Extrapolation of CARB data[11]
4. NPCA marine paint sales
5. Ratio of VOC emissions to antifoulant use

BIBLIOGRAPHY

1. Booz, Allen & Hamilton Inc., "Surface Coating in the Ships and Boats Industry," U.S. EPA RTP, North Carolina Sept. 1978.

2. CENTEC Corp., "Contractor Report for the Development of Effluent Limitation Guidelines for Paint Application Processes Used in the Mechanical and Electrical Products Industries," U.S. EPA, Control #68-02-2581, July 1979.

3. Curtis, George H., "Experiences with a Sophisticated Advanced Cleaning and Coating System," Shipcare '80 Conference, Lisbon, Portugal.

4. Development Document for Proposed Effluent Limitations Guidelines and Standards for the Shipbuilding and Repair Point Source Category, Environmental Protection Agency, Effluent Guidelines Division, December 1979.

5. Federation Series on Coatings Technology, Units 1-25, Federation of Societies for Paint Technology, Philadelphia, Pa., 1965-1978.

6. Huber, Joan E., editor, "The Kline Guide to the Paint Industry," fifth edition, Charles H. Kline & Co., Fairfield, N.J., 1978.

7. Pickering, J. Robert, "Current State of Water-Borne Coating Technology," Metal Finishing, Vol. 76, No. 1, pp. 70-74, January 1978.

8. Principal Shipbuilding and Repair Facilities of the United States (By Coastal Areas and Port Groupings), U.S. Departments of Defense and Commerce, Office of the Coordinator for Ship Repair and Conversion, September 1978.

9. Report on Survey of U.S. Shipbuilding and Repair Facilities, U.S Department of Commerce, Maritime Administration, 1979.

10. Shreve, R. Norris, "Chemical Process Industries," third edition, McGraw-Hill Co., N.Y., 1967.

BIBLIOGRAPHY
(Continued)

11. State of California Air Resources Board, "Consideration of a Proposed Model Rule for the Control of Volatile Organic Compounds from Marine Coating Operations," June 29, 1978.

12. Fairbairn, Robert, "Airless Electrostatic for Aircraft," Finishing Industries, Vol. 4, No. 10, October 1980.

GLOSSARY

ADDITIVES	Any substances, aside from pigment, binder, or solvent, introduced to influence the qualities of paint. They include anti-skinning, anti-sagging, anti-settling agents, preservatives, fungicides, biocides, etc. Usually, the total concentration will be less than 1 percent.
ANTIFOULANT	A chemical additive in paint that controls marine growth on a ship's hull.
BEAM	The width of a ship at its widest point.
BINDERS (RESINS)	The bulk of the film-forming ingredients which bind or cement both the pigment particles together and the paint itself to the material to which it is applied.
BIOCIDES	Compounds that are intended to destroy living organisms. In paints they are considered additives.
BOOTTOP	A paint used on the boottopping to prevent corrosion and fouling.
BOOTTOPPING	The part of a ship's hull between the light load water line and the heavy load water line.
CATALYST	A material that affects the rate of a chemical reaction (usually by providing a reaction site) without itself being chemically altered during the course of the reaction.
CURING	The conversion of the paint film into a solid layer by the use of heat, radiation, or reaction with chemical additives.
DRYDOCK	A dock that is kept dry for use during the construction or repairing of ships.

GLOSSARY
(Continued)

DRYING OILS	Water insoluble liquids that readily absorb oxygen from the air and polymerize to form a relatively hard, tough, elastic substance when applied as a thin film; example: linseed and tung oils.
EMULSIONS	Two or more immiscible liquids, generally existing as a colloidal system, such as oil in water, in which small droplets of one liquid are dispersed uniformly through a second continuous phase.
FLOATING DRYDOCK	A dock that floats on water and can be partly submerged to permit a ship to enter it and afterward floated to raise the ship high and dry as in a drydock.
GRAVING DOCK	A drydock consisting of an enclosure openly adjoining a waterway from which it may be separated by a watertight barrier that is capable of being pumped dry when so separated and which is used especially for cleaning the underwater parts of a ship.
HIGH SOLIDS COATINGS	Liquid conventional finishes that are between 45 and 95 percent solids (by weight). The most common application is of paint of 40 to 80 percent solids content (by weight).
HUMIDITY	A measure of the moisture content of air.
LACQUERS	Coatings that dry primarily by evaporation of solvent rather than by chemical reactions between paint components and/or air.
LATEX PAINT	An aqueous colloidal dispersion coating containing binder (resin) particles produced by emulsion polymerization.
MARINE RAIL	Inclined tracks extending into the water so that a ship can be hauled up on a cradle or platform for cleaning or repairs.
MINERAL SPIRITS	Refined petroleum distillates of low aromatic hydrocarbon content suitable as a solvent or thinner for paints and varnishes with boiling points in the range 149°C to 204°C and flash point around 27°C.

GLOSSARY
(Continued)

OIL BASE PAINTS	Paint containing drying oils as binders that dry by air-induced crosslinking, where oxygen is consumed.
OVERSPRAY	Paint that misses the workpiece in spray coating facilities.
PAINTS	Uniformly dispersed substances that are applied in a thin layer and convert to a solid film on the surface of a workpiece for the purpose of protection, decoration, and/or identification.
PIGMENTS	Small, hard particles dispersed in paint that determine its color, hue, reflectivity, corrosion resistance, hiding power, strength, adhesion properties, and/or viscosity, etc.
PLASTICIZERS	Low molecular weight liquids with high boiling points that, when added to paint, do not evaporate but, rather, improve its flexibility, adhesive power, chip resistance, and formability. Considered an additive.
POLYMERS	Literally meaning many units, are long chain, complex molecules produced by the combination of many fairly simple molecules.
PRIMERS	Initial surface coatings, applied to the surface of a workpiece to provide adequate adhesion to new surfaces or to increase the compatability of the surface for a topcoat.
RESINS	See BINDERS.
SHAVE-AND-A-HAIRCUT	A colloquial expression used to describe the act of blasting and painting a ship's hull.
SOLVENT	A substance capable of dissolving another substance, thus forming a uniformly dispersed solution. In paint, it is the liquid, usually volatile, that acts as the dispersion medium for the film-forming, nonvolatile binders and pigment and at the same time controls the consistency of the coating, making it suitable for application.
SOLVENT-BORNE (BASE) PAINT	Coatings in which an organic liquid (solvent) is used to disperse the binders and pigments.

GLOSSARY
(Continued)

THERMOPLASTIC	In this study, taken to mean the ability to be softened by heat and to be resolidified upon cooling.
THERMOSETTING	The property of being able to undergo a chemical reaction by the action of heat, catalyst, or radiation that causes a substance to become permanently hard and rigid.
THINNER	A type of organic solvent that reduces the viscosity of a paint, varnish, or lacquer to appropriate working consistency, by having active solvent power on the dissolved resin.
TOP COAT (FINISH COAT)	The final coating intended to be applied to a workpiece, usually following a primer, undercoat, or surfacer.
UNDERCOAT	Any coating that is applied prior to the topcoat.
VM&P NAPTHA	Varnish Maker's and Painter's Naptha is a fraction of petroleum distillate, consisting of both aromatics and aliphatic hydrocarbons, used as paint or varnish thinner with narrow boiling point range of 93°C to 149°C and flash point of 10°C.
WATER-BORNE COATINGS (WATER-BASED COATINGS)	A type of coating in which water acts as the primary solvent to disperse and suspend the pigment and binder material.